

Phytotoxicology Investigation in the Vicinity of Algoma Steel Inc. Sault Ste. Marie - 2002

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Background:

Algoma Steel Incorporated is an integrated primary iron and steel producer located on the St. Mary's River in Sault Ste. Marie, Ontario. Integrated mills produce steel in blast furnaces where iron ore is mixed with coke and the coke is burned under controlled conditions so that carbon monoxide is produced. This carbon monoxide chemically reduces the ore, consisting primarily of iron oxides, to metallic iron. Limestone added to the furnace provides an additional source of carbon monoxide as well as acting as a flux to fuse with silicates in the ore. The resulting calcium silicate floats to the top of the molten iron and is drawn off as slag.

A critical material in steel making is the coke. Coke is produced by heating coal to high temperatures and distilling off the volatile components of the coal. The remaining material consists primarily of carbon and is known as coke. Coke provides the high heating value to smelt the iron ore and is also the source of carbon in steel.

Integrated mills produce their own coke in coke ovens. The ovens consist of narrow vertical chambers known as 'batteries'. The heat to distill the coal is generated by burning gases in spaces between adjoining chambers. Volatile compounds released as the coal is distilled are condensed to produce coal tar while the non-condensed gases are recovered and burned to distill fresh charges of coal.

Polycyclic Aromatic Hydrocarbons:

During coke production there are inevitable emissions of volatilized coal tar or of coal gas to the atmosphere. Major constituents of coke oven emissions are a class of organic compounds known as polycyclic aromatic hydrocarbons (PAHs). PAHs consist of three or more fused aromatic rings. Some consist only of carbon and hydrogen atoms while others have other atoms substituting carbon in the benzene ring or functional groups substituting hydrogen atoms. Consequently, it is possible to have a great diversity of PAHs. It should be noted that PAHs are not necessarily constituents of coal but can be formed during the coal distillation process.

The boiling points of PAHs are usually high enough so that they will not persist in the atmosphere in vapour form, but will condense onto particulates acting as condensation nuclei. Consequently, the dispersion and deposition characteristics of PAHs is dependant on the behaviour of the particulate nuclei. Small particles will be transported greater distances than larger particles and can theoretically contain a higher mass to volume ratio of adsorbed PAHs. However, since the greater the dispersion distance the greater the dilution, ambient air concentrations of PAHs, either in vapour or particulate form, are invariably higher near a point source.

The primary concern about PAHs is that some are considered probable human carcinogens. One of these, benzo(a)pyrene, has been the subject of considerable toxicological research and is the only PAH compound for which Ontario has an interim ambient air standard. This concentration, which is 1.1 nanograms per cubic metre of outdoor ambient air per 24 hours, is regularly exceeded at a MOE monitoring station located near a residential neighbourhood near the Algoma Steel complex.

Investigation Procedures:

The investigation which is the subject of this report follows one conducted in 1998 and reported in the MOE Phytotoxicology report SDB-075-3511-1999. The 1998 investigation concluded that Algoma Steel was a source of airborne PAHs, but that the soil sampling in the adjacent residential neighbourhood was of insufficient intensity to attribute elevated soil PAH concentrations at some sampling sites to Algoma Steel. Consequently, in 2002 a supplemental investigation was requested by the MOE Sault Ste. Marie District Office to delineate the extent and degree of soil contamination by PAHs in this neighbourhood which could be used to determine if there might be a human health concern related to the soil contamination.

The investigation was conducted on July 31, 2002 and consisted of collections of surface soil samples at 20 locations in the residential neighbourhood immediately northwest of Algoma Steel. These sampling locations were located primarily on individual front, side or rear yards of residential properties. One location was at a municipal park. The figure below shows the distribution of sampling locations.

Figure 1: Soil Sampling Locations - Algoma Steel Inc., Sault Ste. Marie, July 31, 2002



Before a particular yard was committed as a sampling location, the occupant was asked if the soil in the yard had been disturbed by landscaping activity. The objective was to select locations that contained soil subjected to a long period of PAH deposition. Prior to sampling, all sampling equipment that would be in contact with the sample was washed with a high-phosphate detergent, rinsed with deionized water, and then successively rinsed with acetone and hexane. The sample containers consisted of amber glass jars with aluminum foil lids. These containers were previously washed with a detergent solution followed by several deionized water rinses and were provided by the MOE Laboratory Services Branch.

A sampling location consisted of the whole of the sodded portion of the yard, or an area about 10 metres by 10 metres if the yard was particularly large. Ten cores of soil to a depth of 2.5 centimetres were removed over a grid pattern with a soil coring device consisting of a hollow, two centimetre diameter, stainless steel tube fitted with a cutting tip. The individual cores were placed into a stainless steel bowl, dis-aggregated, homogenized and transferred to a labelled glass sample jar.

The sampling depth selected for this investigation was shallower than the 0-5 centimetre depth sampled in 1998. The objective was to maximise the probability of quantifying PAH concentrations by collecting the uppermost layer of soil where PAHs deposited from the air would be present. This reduced the potential diluting influence of deeper, less contaminated soil.

All samples were forwarded to the MOE Laboratory Services Branch for determination of PAH concentrations by gas chromatography - mass spectrometry (GC-MS).

Results:

Table 1 contains the concentrations of 16 PAH compounds in the surface soil collected during this investigation. The data are reported in nanograms per gram, also known as parts per billion, on a dry weight basis. The last two columns in this table contain criteria from the MOE *Guideline for Use at Contaminated Sites in Ontario*. The column labelled Table B contains the generic effects-based criteria commonly known as Table B. The column labelled Table F contains the background-based criteria for Ontario soil. The Appendix discusses the *Guideline* rationale.

Table 1: PAHs (ng/g dw) in Surface Soil (0-2.5 cm) near Algoma Steel, SSM - July 31, 2002

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Naphthalene	280	160	140	80 <T	140	140	80 <T	140
Acenaphthylene	40 <T	20 <=W	20 <=W	20 <=W	60 <T	60 <T	20 <=W	40 <T
Acenaphthene	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W
Fluorene	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	40 <T	20 <=W	20 <=W
Phenanthrene	340	240	300	140	500	480	260	400
Anthracene	20 <=W	20 <=W	40 <T	20 <=W	80 <T	180	40 <T	40 <T
Fluoranthene	520	400	520	220	1400	1200	780	740
Pyrene	440	320	420	180	1100	1000	660	600
Benzo(a)anthracene	240	180	200	100	560	540	380	340
Chrysene	360	260	300	160	720	700	420	480
Benzo(b)fluoranthene	460	340	420	220	980	940	580	620
Benzo(k)fluoranthene	140	100	140	60 <T	340	320	200	200
Benzo(a)pyrene	200	160 <T	200	120 <T	520	520	320	280
Benzo(g,h,i)perylene	240	160 <T	200	120 <T	480	480	240	280
Dibenzo(a,h)anthracene	40 <=W	40 <=W	40 <=W	40 <=W	120 <T	120 <T	80 <T	80 <T
Indeno(1,2,3-c,d)pyrene	240	160 <T	200	120 <T	520	480	280	280
	Site 9	Site 10	Site 11	Site 12	Site 13	Site 14	Site 15	Site 16
Naphthalene	60 <T	80 <T	140	220	160	60 <T	140	120
Acenaphthylene	20 <=W	60 <T	40 <T	40 <T	20 <=W	20 <=W	40 <T	40 <T
Acenaphthene	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W
Fluorene	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	20 <=W	40 <T	20 <=W
Phenanthrene	140	300	320	400	300	160	500	300
Anthracene	20 <=W	20 <=W	40 <T	40 <T	20 <=W	20 <=W	80 <T	40 <T
Fluoranthene	320	760	820	680	460	320	900	720
Pyrene	260	600	640	540	360	260	700	540
Benzo(a)anthracene	120	340	340	280	180	140	360	280
Chrysene	260	440	460	440	300	200	560	520
Benzo(b)fluoranthene	360	680	640	580	400	260	620	640
Benzo(k)fluoranthene	100	220	200	180	120	80 <T	220	200
Benzo(a)pyrene	120 <T	320	320	240	200	120 <T	320	280
Benzo(g,h,i)perylene	160 <T	320	280	240	200	120 <T	320	240
Dibenzo(a,h)anthracene	40 <=W	80 <T	80 <T	80 <T	40 <=W	40 <=W	80 <T	80 <T
Indeno(1,2,3-c,d)pyrene	160 <T	360	280	240	200	120 <T	320	280
	Site 17	Site 18	Site 19	Site 20	Table B		Table F	
Naphthalene	120	180	140	60 <T	40000		90	
Acenaphthylene	60 <T	40 <T	20 <=W	20 <=W	100000		80	
Acenaphthene	20 <=W	20 <=W	20 <=W	20 <=W	1000000		70	
Fluorene	20 <=W	20 <=W	20 <=W	20 <=W	350000		120	
Phenanthrene	340	380	220	120	40000		690	
Anthracene	20 <=W	40 <T	20 <=W	20 <=W	28000		160	
Fluoranthene	860	700	400	200	40000		1100	
Pyrene	720	560	300	160	250000		1000	
Benzo(a)anthracene	360	280	180	100	40000		740	
Chrysene	500	420	280	140	12000		690	
Benzo(b)fluoranthene	760	660	340	200	12000		470	
Benzo(k)fluoranthene	260	220	100	60 <T	12000		480	
Benzo(a)pyrene	360	280	120 <T	80 <T	1200		490	
Benzo(g,h,i)perylene	360	280	160 <T	120 <T	40000		680	
Dibenzo(a,h)anthracene	80 <T	80 <T	40 <=W	40 <=W	1200		160	
Indeno(1,2,3-c,d)pyrene	360	320	160 <T	120 <T	12000		380	

Discussion:

The purpose of this investigation was not to determine whether the Algoma Steel coke ovens were a source of PAHs. This has been adequately determined by ambient air monitoring and by the 1998 Phytotoxicology soil and tree foliage sampling. Also, the fact that Table F criteria are frequently exceeded as indicated by shading in Table 1, demonstrates a source of PAHs impacting the soil. Rather, this investigation tries to delineate the intensity and extent of soil contamination by PAHs in the residential neighbourhood that is in very close proximity to the coke ovens.

When the concentrations of the PAHs reported in Table 1 are compared to the Table B criteria, it is evident that these concentrations are well below the effects-based criteria. Even the highest benzo(a)pyrene concentration is still less than half its respective criterion value. Benzo(a)pyrene is the most toxic PAH and therefore has the lowest generic criterion.

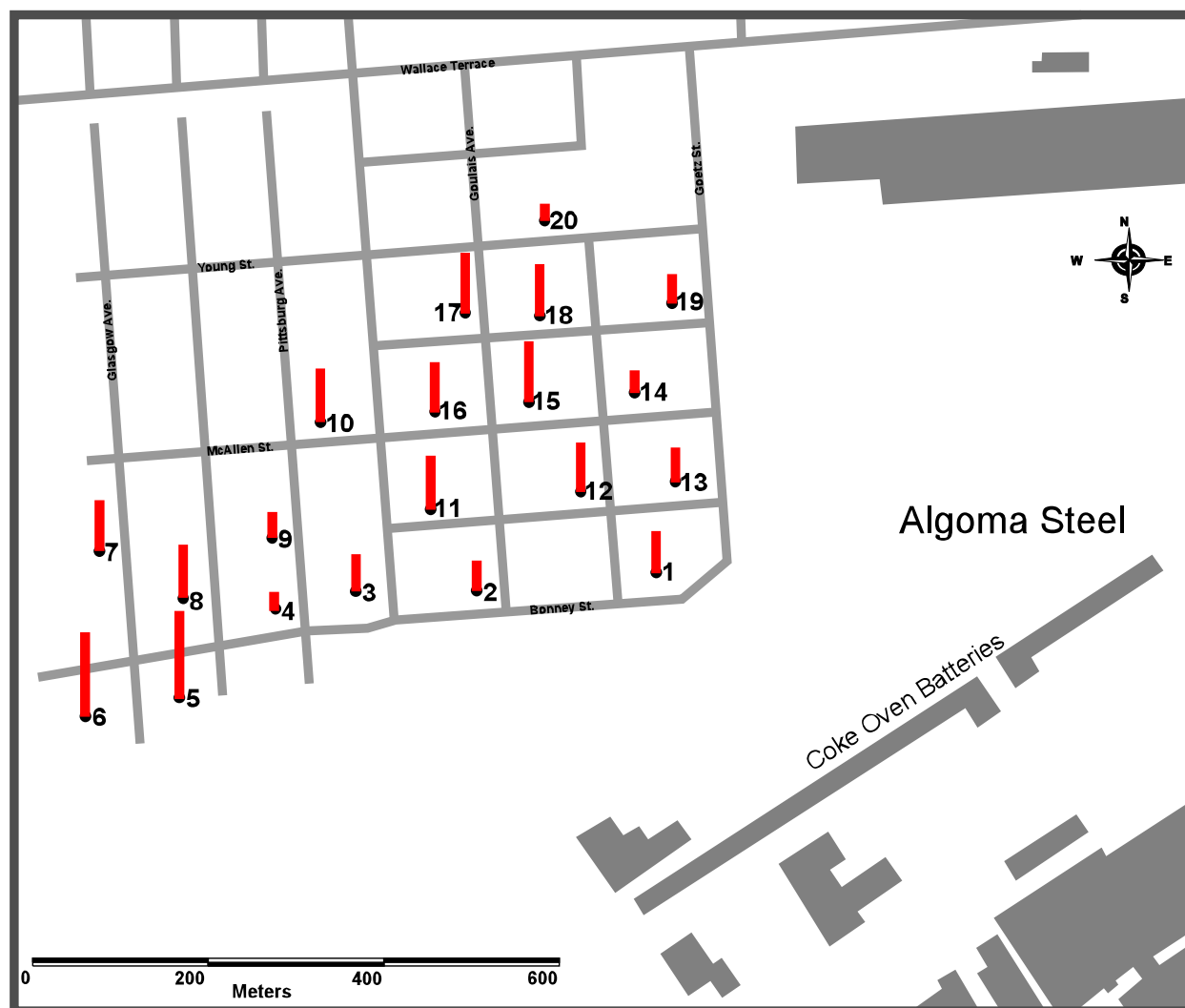
Samples were collected from a series of very similar locations, namely residential yards that, as well as could be determined, had not been disturbed and would have been exposed to atmospheric deposition by emissions from the coke ovens. Therefore the data lent itself to an evaluation of the areal extent of PAH contamination in this neighbourhood. Since none of the soil concentrations exceeded the generic effects-based criteria, the concentrations of the 16 PAH compounds determined for each sample were simplified by summing the reported concentrations to derive "total" PAH concentrations. This total is of course only for the 16 compounds. Also, the qualifiers <T and <=W were disregarded. There is no MOE soil guideline for "total" PAHs.

These "total" concentrations as reported in Table 2 were then plotted as a histogram. However, instead of showing these data in a conventional graph format, the individual data bars have been superimposed on the map showing the sampling locations, with the base of each bar positioned on the site marker. Figure 2 provides a visual representation of the PAH concentrations in this neighbourhood as determined by this investigation.

Table 2: "Total" PAH Concentrations (ng/g dw) in Surface (0-2.5 cm) Soil

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8	Site 9	Site 10
"Total" PAH	3600	2600	3180	1640	7560	7220	4380	4560	2180	4620
	Site 11	Site 12	Site 13	Site 14	Site 15	Site 16	Site 17	Site 18	Site 19	Site 20
"Total" PAH	4640	4240	3000	1960	5220	4320	5200	4480	2520	1480

When Figure 2 is examined, there does not appear to be a clear PAH distribution pattern through this neighbourhood. In other words, locations that are closer to the coke ovens, such as Site 1, do not necessarily have the highest concentrations, nor do more distant locations such as Site 17 have the lowest. While PAH deposition from the coke ovens is indicated, the residual effect of this deposition at a particular location, as measured by the soil concentrations, varies. This variability may be due to property specific factors. Foremost among these would be landscaping activity performed by present or past occupants. Other factors that might contribute to the observed concentrations may be microbiological activity that degrades PAHs, or the sheltering influence of buildings or trees that affect what reaches the ground.

Figure 2: “Total” Soil PAH Conc. - Algoma Steel Inc., Sault Ste. Marie, July 31, 2002**Conclusions:**

The objective of this investigation was to determine the degree and areal extent of PAH contamination of soil in the residential neighbourhood adjacent to the coke ovens of Algoma Steel. Since the Table F criteria of the *Guideline for Use at Contaminated Sites in Ontario* were exceeded, soil in the neighbourhood adjacent to Algoma Steel has been impacted by a source or sources of PAHs. However, the concentrations of PAHs in the surface soil of the residential properties are less than the generic effects-based criteria contained in Table B of the MOE *Guideline*. Therefore, there should be no adverse ecological or human health effects due to the marginally elevated PAHs detected in the soil of some residential properties northwest of Algoma Steel.

The areal extent of this contamination could not be clearly defined. The previous 1998 investigation, which consisted of sampling locations over a much broader area, revealed soil PAH levels of similar magnitude in various locations well removed from the coke ovens.

Although the Algoma Steel coke ovens are a known source of PAHs in the air, there was no apparent gradient of increasing soil PAH levels closer to Algoma, and therefore it is not possible to separate the coke oven contribution to soil PAH concentrations from that of other PAH sources in the urban environment. These could include emissions from vehicles, particularly with diesel engines, erosion of coal tar based roofing materials, or use of coal tar based products such as creosote at the property.

While more intensive sampling might shed more light on the relative contributions of PAHs from the coke ovens, given that the sampling conducted to date has shown that soil concentrations do not exceed effects-based criteria even in the areas likely to have been most significantly impacted by Algoma, additional sampling is not warranted at this time.

Appendix

Derivation and Significance of the MOE Soil Remediation Criteria (Clean-up Guidelines)

The MOE soil clean-up *Guidelines* have been developed to provide guidance for cleaning up contaminated soil. The *Guidelines* are not legislated Regulations. Also, the *Guidelines* are not action levels, in that an exceedence does not automatically mean that a clean-up must be conducted. The *Guidelines* were prepared to help industrial property owners decide how to clean-up contaminated soil when property is sold and/or the land-use changes. Most municipalities insist that contaminated soil is cleaned up according to the MOE *Guidelines* before they will approve a zoning change for redevelopment, therefore, even though the *Guideline* is voluntary most industrial property owners and developers are obliged to use it. For example, the owner of an industrial property who plans to sell the land to a developer who intends to build residential housing can use the *Guideline* to clean up the soil to meet the residential land-use criteria. In this way previously-contaminated industrial land can be re-used for residential housing without concern for adverse environmental effects.

The *Guideline* contains a series of Tables (A through F), each having criteria for soil texture, soil depth, and ground water use for various land-use categories (eg, agricultural, residential, industrial). Table F *criteria* reflect the upper range of background concentrations for soil in Ontario. An exceedence of Table F indicates the likely presence of a contaminant source. Tables A through E *criteria* are effects-based and are set to protect against the potential for adverse effects to human health, ecological health, and the natural environment, whichever is the most sensitive. By protecting the most sensitive parameter the rest of the environment is protected by default. The *Guideline criteria* take into consideration the potential for adverse effects through direct contact, and through contaminant transfer from soil to indoor air, from ground water or surface water through release of volatile gases, from leaching of contaminants in soil to ground water, or from ground water discharge to surface water. However, the *Guideline criteria may not* ensure that corrosive, explosive, or unstable soil conditions will be eliminated.

If the decision is made that remedial action is needed, the *criteria* in Tables A to F of the *Guideline* can be used as clean-up targets. In some cases, because of economic or practical reasons, it may not be possible to clean up a site using the generic *criteria* in Tables A to F. The *Guideline* provides a process, called a *site specific risk assessment*, which is used to evaluate the soil contamination with respect to conditions that are unique to the contaminated site. In a *site specific risk assessment* the proponent examines all the potential pathways through which the contamination may impact the environment and must demonstrate that because of conditions unique to that site the environment and human health will not be adversely effected if contamination above the generic *criteria* in Table A to E is left in place.

When contamination is present and a change in land-use is not planned, for example residential properties and public green spaces near a pollution source, the *Guideline* may be used in making decisions about the need for remediation. This is different from the previously described situation where a company that caused contamination on their own property decides to clean up the soil, usually at the insistence of the municipality who will not approve a zoning change unless remediation is conducted. Decisions on the need to undertake remedial action

when the *Guideline criteria* are exceeded **and** where the land-use is not changing are made on a site by site basis using *site specific risk assessment* principals and are usually contingent on the contaminants having caused an adverse environmental effect or there is a demonstrated likelihood that the contamination may cause an adverse effect. Because of the long history of industrial operation and our practice of living close to our work place the soil in many communities in Ontario is contaminated above the effects-based *criteria* in the MOE *Guidelines*. In practice, remediation of contaminated soil on privately-owned residential property and public green spaces has only been conducted in communities when the potential for adverse health effects has been demonstrated.

The soil clean-up *Guidelines* were developed from published U.S. EPA and Ontario environmental data bases. Currently there are criteria for about 25 inorganic elements and about 90 organic compounds. Criteria were developed only if there were sufficient, defensible, effects-based data on the potential to cause an adverse effect. All of the criteria address human health and aquatic toxicity, but terrestrial ecological toxicity information was not available for all elements or compounds. The development of these clean-up *Guidelines* is a continuous program, and criteria for more elements and compounds will be developed as additional environmental data become available. Similarly, new information could result in future modifications to the existing *Guidelines*.

For more information on the MOE's soil clean-up *Guidelines* please refer to the *Guideline for Use at Contaminated Sites in Ontario. Revised February 1997*, Ontario Ministry of Environment and Energy, PIBs 3161E01, ISBN 0-7778-6114-3. This document is also available on the MOE web site at www.ene.on.ca, look under *Contaminated Sites: Clean-up Guideline*.